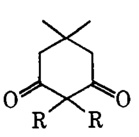
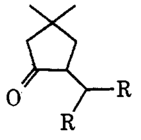
The SFOR[6,7] cmr spectrum of the previously prepared **1a** showed two doublets, two quartets, and four singlets or triplets derived from the eight reported[2] saturated carbon absorptions (Table I). The two doublets must arise from CH groups; hence, the compound cannot be **1a**. Furthermore, the benzylic methylene protons which gave a broadened asymmetric doublet at 60 MHz turned into well-resolved multiplets consisting of at least ten lines at 220 MHz (Figure 1) in which the smallest splittings were 6 Hz. This part of the spectrum corresponds to expectations for a $(C_6H_5CH_2)_2CH-$ grouping where the benzyl groups are magnetically nonequivalent.

The literature has several examples of anomalous reductions of β-diketones.[8,9] Clemmensen reduction of dimedone (**2a**) yields **3a**;[8] in an analogous manner, reduction of **2b** might produce **3b**. This compound could subsequently be converted to **4** upon further reaction, as described earlier.[2]

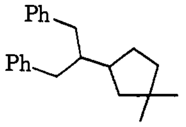


2



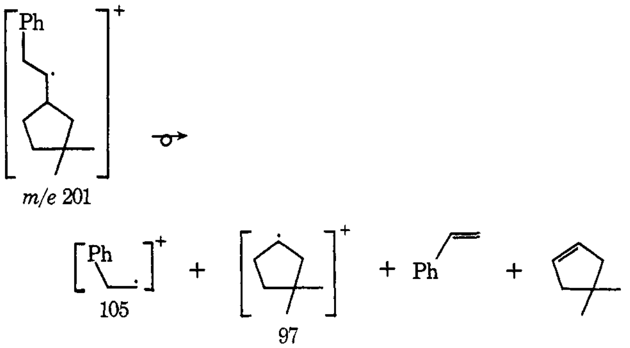
3

a, R = H
b, R = $C_6H_5CH_2$



4

Structure **4** is consistent with the cmr and pmr data previously assigned to **1a**.[2] The two methyl groups and the pair of benzylic methylenes are both diastereotopic and their resonances are not expected to coalesce upon heating or cooling. Because there are ten different carbon atoms in **4**, but only eight cmr signals were observed, some signals must be overlapping. On the basis of the SFOR data from Table I, the accidental degeneracies appear to involve the five different methylene moieties and/or the two quaternary carbons.



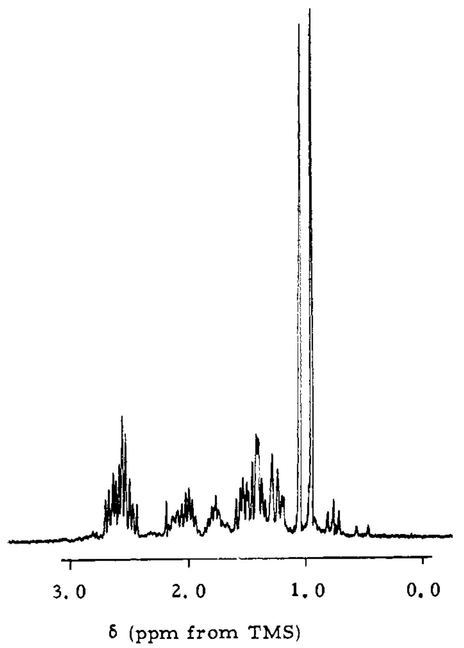


Figure 1. Aliphatic region of 220-MHz pmr spectrum of **4**.

The previously reported mass spectral data[2] are completely in accord with **4**. While both **1a** and **4** can produce ions at *m/e* 91 and 201 by benzyl cleavage, only the *m/e* 201 fragment derived from **4** can undergo straightforward decomposition to yield the observed ions at *m/e* 105 and 97.

We conclude that there is no experimental evidence at this time that dibenzylcyclohexanes exhibit other than normal inversion barriers.

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[6] H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 7445 (1969); SFOR, single frequency off resonance.

[7] M. Jautelat, J. B. Grutzner, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **65**, 288 (1970).

[8] N. J. Cusack and B. R. Davis, *J. Org. Chem.*, 30, 2062 (1965).

[9] W. Reusch and D. B. Priddy, *J. Amer. Chem. Soc.*, **91**, 3677 (1969).

[10] National Institutes of Health Postdoctoral Fellow, 1971–1972.

Ring Nonrigidity in the Chair Conformation of 1,1-Dibenzyl-4,4-dimethylcyclohexane

Sir:

It was recently reported[1] that the presence of geminal benzyl groups in 1,1-dibenzyl-4,4-dimethylcyclohexane (**4**) gives rise to an unprecedented increase in the magnitude of the cyclohexane ring inversion barrier (>20 kcal/mol), providing "direct evidence of the greater mobility of the boat as compared to the chair form."[1] We now wish to report that the properties described

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[1] H. Kwart, M. C. Rock, R. Sánchez-Obregón, and F. Walls, *J. Amer. Chem. Soc.*, **94**, 1759 (1972).

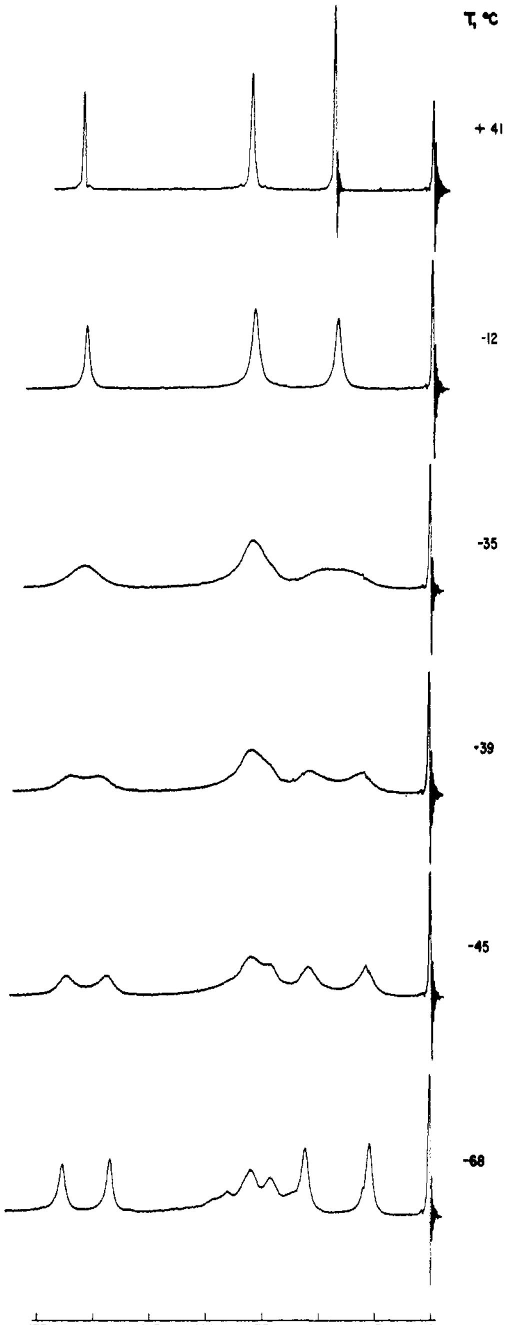


Figure 1. ^1H nmr spectral tracings (aliphatic region only) for **4** (*ca.* 20% in CS_2 solution, 60 MHz) at different temperatures. The scale is in hertz and is relative to internal TMS.

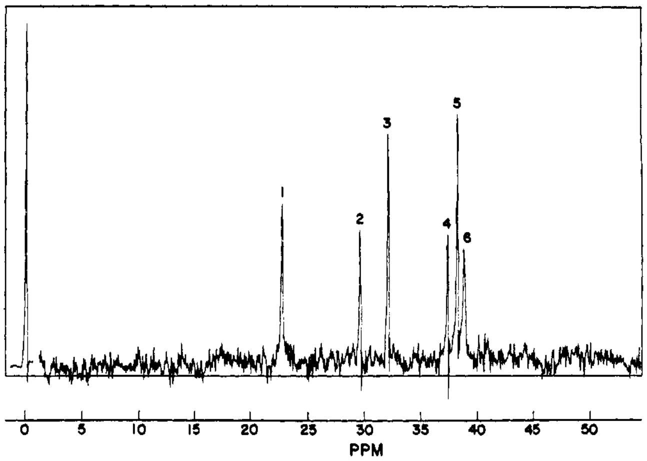
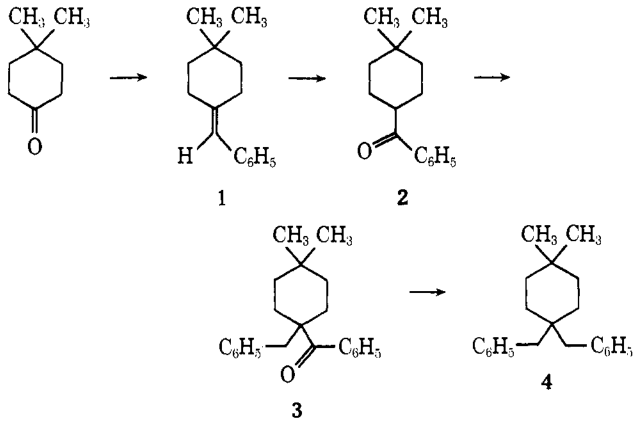


Figure 2. ^{13}C proton-decoupled nmr spectral tracing (aliphatic region only) for **4** (*ca.* 1 *M* in dioxane + 5% C_6F_6, 22.63 MHz). The scale is in parts per million relative to dioxane. Peaks 2 and 4 have been identified as absorptions due to quaternary carbons by noise off-resonance decoupling and continuous wave off-resonance decoupling experiments. See, for example, E. Wenkert, A. O. Clouse, D. W. Cochran, and D. Doddrell, *J. Amer. Chem. Soc.*, **91**, 6879 (1969); W. O. Crain, Jr., W. C. Wildman, and J. D. Roberts, *ibid.*, **93**, 990 (1971), and references cited therein.

Scheme I



for the previously prepared substance[1,2] are not those of **4** and that the ring inversion barrier for **4**, prepared by an independent route (Scheme I), is only *ca.* 12 kcal/mol.

Reaction of 4,4-dimethylcyclohexanone[3] with benzylidenetriphenylphosphorane[4] afforded (36%) benzylidene-4,4-dimethylcyclohexane (**1**)[5] [bp *ca.* 125° (4 mm); $\delta^{\rm TMS}_{\rm CDCl_3}$ 0.95 (s, CH_3), 1.15–1.60 (m, CH_2), 2.13–2.53 (m, CH_2), 6.12–6.25 (m, CH), 7.08–7.28 (m, C_6H_5)], which was converted (50%) to the ketone **2** by reaction with diborane in tetrahydrofuran, followed by two-phase oxidation with chromic acid.[6] The ketone **2** [mp 63–65°; $\delta^{\rm TMS}_{\rm CDCl_3}$ 0.96 (s, CH_3), 1.10–2.15 (m, CH_2), 2.92–3.50 (m, CH), 7.30–8.02 (m, C_6H_5)] was treated sequentially with sodium hydride and benzyl bromide in boiling toluene to provide (55%) ketone **3** [mp 76–78°; $\delta^{\rm TMS}_{\rm CDCl_3}$ 0.79 (s, CH_3), 0.87 (s, CH_3), 0.95–2.40 (m, CH_2), 3.10 (s, $CH_2C_6H_5$), 6.95–7.50 (m, C_6H_5)], which was converted to **4** by either Wolff–Kishner reduction[7] (35%) or by hydrogenolysis over palladium chloride[8] (85%). Samples for nmr analyses, purified by chromatography on silica gel followed by kugelrohr distillation, were homogeneous (glpc and tlc).

The previously described[1,2] ^1H nmr spectrum exhibited "two widely separated, sharp, methyl singlets," "two distinct benzylic methylene absorptions," and a "broad band of unresolved multiplets ranging from

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(2) M. C. Rock, F. Walls, and H. Kwart, *Bol. Inst. Quim. Univ. Nac. Auton. Mex.*, 22, 33 (1970); 21, 97 (1969).

(3) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 1347 (1963).

(4) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

(5) Acceptable (±0.3%) elemental analyses were obtained for all new compounds (1–4). Mass spectra were likewise consistent with the assigned structures.

(6) H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2951 (1961).

(7) The Nagata-Itazaki modification was employed. W. Nagata and H. Itazaki, *Chem. Ind. (London)*, 1194 (1964).

(8) J. Rothe and H. Zimmer, *J. Org. Chem.*, **24**, 586 (1959).

92 to 44 Hz." An eight-line ^{13}C nmr spectrum was previously reported, which "completely verifies the rigidity of the ring since it establishes beyond cavil the doubling of methyl and benzylic methylene carbon resonances."[1] Both spectra are distinctly different from those obtained for hydrocarbon **4**, which are displayed in Figures 1 and 2.[9,10] The mass spectrum of the hydrocarbon **4** (prepared by Scheme I) (M^+ *m/e* 292.219200, major ions at *m/e* 201, 200, 109, 105, 97, and base peak 91) is consistent with the assigned structure (calcd M^+ *m/e* 292.219090).

The ^1H nmr spectrum of **4** is temperature dependent (Figure 1). Use of the Gutowsky-Holm equation[11] to obtain rate constants for the site exchange of the methyl group protons and of the benzylic methylene group protons (Figure 1) leads to values for $\Delta G^{\ddagger}$ of *ca.* 11.8 and 11.9 kcal/mol, respectively. These values fall within the normal range of values determined for ring inversion in similarly substituted cyclohexanes.[12]

While the present results do not clarify the nature of the substance obtained by the earlier authors[1,2] and presumed by them to be **4**,[12a] they do establish beyond cavil that **4** does not maintain an "immobile chair conformation" as claimed.[1] By the same token, the rationale advanced[1] to account for the "exceedingly rigid chair" of **4** must be abandoned.

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(9) ^1H nmr: $\delta_{CS_2}^{TMS}$ 0.71 (s, CH_3), 1.31 (m, CH_2), 2.53 (s, $CH_2C_6H_5$), and 6.87–7.25 (m, C_6H_5). Essentially the same spectrum was observed using $CDCl_3$ or $CFCl_3$ as solvent.

(10) ^{13}C nmr (excluding the unsaturated carbon region): δ ^{13}C from dioxane 38.74, 38.14, 37.27, 32.00, 29.49, and 22.66 ppm at *ca.* 40°. These values may be corrected to chemical shifts from benzene by the following equation: δ (from C_6H_6) = δ (from dioxane) + 61.44 ppm.

(11) This method of calculation of $\Delta G^{\ddagger}$ is judged to be sufficiently accurate for the present case. See, for example, D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(12) I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, 4, 71 (1971).

(12a) NOTE ADDED IN PROOF. After the present work was completed, we were informed that this question has since been answered by R. H. Levin, J. D. Roberts, H. Kwart, and F. Walls, *J. Amer. Chem. Soc.*, **94**, 6856 (1972). We thank Professor Roberts for agreeing to publish these results concurrently with ours.

(13) Public Health Service Predoctoral Fellow, 1969–1972.

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Dinitrogen Complexes of Molybdenum(I)

Sir:

We wish to report the first examples of a molybdenum(I) cation containing coordinated dinitrogen. The only other reported molybdenum(I)–dinitrogen complex is $MoCl(N_2)(diphos)_2$[1] (where diphos = 1,2-bis-diphenylphosphinoethane).

The addition of solid $Mo(N_2)_2(diphos)_2$[2] (1.0 mmol) to a methanol solution of iodine (3.5 mmol) under dinitrogen produced a red precipitate I, formulated as $[Mo(N_2)_2(diphos)_2]^+I_3^-$, in 90% yield. *Anal.* Calcd for I: C, 47.0; H, 3.6; N, 4.2; I, 28.9. Found: C, 47.3; H, 3.7; N, 3.4; I, 28.9. The complex I is stable in dry air but decomposes readily in solution. In fact the preparation of I could only be carried out under heterogeneous conditions. Attempts to oxidize $Mo(N_2)_2(diphos)_2$ in benzene with iodine gave products containing no dinitrogen.

The infrared spectrum of I showed a strong absorption at 2043 cm^{-1} due to the $\nu(N\equiv N)$ stretching vibration. The increase of $\nu(N\equiv N)$ from 1976 cm^{-1} for $Mo(N_2)_2(diphos)_2$ to 2043 cm^{-1} for I supports an increase in the formal oxidation state of molybdenum ($Mo^0 \rightarrow Mo^+$).

Magnetic susceptibility measurements of I gave a spin-only value for μ_{eff} (uncorrected for diamagnetism) at 25° of 1.97 BM. This value is comparable to the 1.66 BM value reported for the isoelectronic $[Mo(CO)_2(diphos)_2]I_3$[3] and indicates a spin of $^1/_2$.

I could be reduced to the original $Mo(N_2)_2(diphos)_2$ with sodium amalgam in benzene or tetrahydrofuran (40 and 45% yields, respectively), under dinitrogen. However, under argon, no dinitrogen-containing product was isolated.

The reversibility of the oxidation of $Mo(N_2)_2(diphos)_2$ was established by cyclic voltammetry. The voltammogram was run with 10^{-3} *F* dimethylformamide solutions containing 10^{-1} *F* tetraethylammonium perchlorate as supporting electrolyte at a platinum electrode. Scans were run in the range +0.43 to −0.65 V *vs.* a standard calomel electrode with a scan time of 10.00 Hz. $Mo(N_2)_2(diphos)_2$ gave an anodic peak potential at −0.20 V on the forward scan and a cathodic peak potential at −0.27 V on the reverse scan. Similarly, $Mo(N_2)_2(arphos)_2$[4] (where arphos = 1-diphenylarsino-2-diphenylphosphinoethane) gave a scan with peaks at −0.19 and −0.26 V, respectively. Controlled potential coulometry and conductivity measurements were unsuccessful due to the extensive decomposition of I in solution, over a period of time.

The infrared, analytical, and magnetic susceptibility data support the formulation of I as *trans*-$[Mo(N_2)_2(diphos)_2]^+I_3^-$. However, an alternative formulation that does not conflict with the observed data is $\{\mu\text{-}N_2\text{-}[Mo(N_2)(diphos)_2]_2\}^{2+}(I_3^-)_2$ (II). *Anal.* Calcd for II: C, 47.4; H, 3.7; N, 3.2; I, 28.9. The bridging dinitrogen and the two terminal dinitrogen ligands in II would have to be linear (mutually trans) to be consistent with the one $\nu(N\equiv N)$ stretching vibration observed in the infrared spectrum. Efforts to locate the $\nu(N\equiv N)$ stretching vibrations in the Raman have been unsuccessful as a result of the rapid loss of dinitrogen due to interaction with the laser light (4880 Å). The $Mo(N_2)_2(diphos)_2$ complex was also oxidized in benzene by hydrogen chloride and by hydrogen bromide to give either $[Mo(N_2)_2(diphos)_2]^+Cl^-$ and $[Mo(N_2)_2(diphos)_2]^+Br^-$ or the analogous dinitrogen dimer of II. The reaction with chlorine yielded no dinitrogen-containing species. Metal ions such as silver(I) and copper(II), which have been used for the

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(1) L. K. Atkinson, A. H. Mawby, and D. C. Smith, *Chem. Commun.*, 157 (1971).

(2) (a) J. Chatt and A. G. Wedd, *J. Organometal. Chem.*, **27**, C15 (1971); (b) M. Hidai, K. Tominari, and Y. Uchida, *J. Amer. Chem. Soc.*, **94**, 110 (1972).

(3) J. Lewis and R. Whyman, *J. Chem. Soc.*, 5486 (1965).

(4) T. A. George and C. D. Seibold, *Inorg. Nucl. Chem. Lett.*, **8**, 465 (1972).